# Observations of Aerosols over Southern California Coastal Waters

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ABSTRACT

To characterize the background aerosol in air off the California coast, observations of suspended particles were made in the summer and fall of 1970 on San Nicolas Island (SNI), located about 130 km west-southwest of Los Angeles. Measurements of the physical and chemical properties of aerosols showed that the particles are a complex mixture of material from marine and continental origins. The Aitken nuclei population averaged 2400 $cm^{-3}$, while the particles $>0.5\ \mu m$ diameter averaged 20–100 $cm^{-3}$. The average total mass concentration of aerosol evaluated from 22 samples was 29.8 $\mu g\ m^{-3}$, but the refined fraction defined as particles $\lesssim 3.5\ \mu m$ diameter was 40% of this level.

The averages of the chemical analysis of 13 samples revealed that 11% of the aerosol sampled at a 200 m height above the ocean was sea salt, while approximately 20% evidently was soil dust, as indicated by silicates. Over 25% of the suspended material was found to be sulfate, nitrate or ammonium, which are constituents believed to be produced primarily from gaseous transformation reactions in the atmosphere.

More than 20% of the sampled material was volatile in nature and is believed to be partly water. The ratio for the average chlorine to sodium concentrations from the analysis of 13 different samples was 2.4 compared with 1.8 for sea water. This high ratio supports other limited results for unpolluted air from offshore sources taken in this geographical region. The anomaly is believed to be linked with chemical reactions transforming gaseous chlorine compounds into condensed material.

Comparison was made between the aerosol sampled on San Nicolas Island and the "natural" background contribution of the Los Angeles smog aerosol, as estimated elsewhere assuming contributions solely from sea salt and soil dust. The calculated background and the composition of the SNI aerosol were qualitatively similar, with the principal differences showing in Ca, Zn, $SO_4^=$ and $NO_3^-$. Further comparison with aerosol analyzed from Pasadena illustrated the major contribution of localized pollution to the chemical properties of the particles, particularly in the concentrations of Mn, Ca, Br, Fe, Pb, $SO_4^=$ and $NO_3^-$.

## 1. Introduction

Recently, considerable interest has developed in determining the natural background of trace constituents of the earth's atmosphere. Such information has become important in the assessment of man's impact on his environment, as well as in the establishment of meaningful air quality criteria. The "natural background" is difficult to define and to evaluate in most cases. At any specific location, the background generally represents a complicated mixture of minute quantities of gas and airborne particles that come from a variety of localized natural sources. On this is superimposed a residue of aged material from natural and anthropogenic sources remaining in the air for long periods of time. As more data become available, it already is recognized that each geographical region has certain unique background features that depend on local sources and patterns of air movement on a large scale.

By characterizing the variations in physical and chemical properties of aerosols sampled well away from major population centers, with accompanying weather patterns, it should be possible to improve assessment of the background aerosol and their contribution to aerosols observed in the cities. This is essentially the approach underlying the observations described here.

Because of its complexity, the atmospheric chemistry of regions along the Southern California coast is of interest. Southern California often experiences conditions of reduced visibility that are sometimes attributed to persistent natural fog in the area. At other times, the haze over Southern California is identified with man's activities and is normally considered as the visible symptom of photochemical smog. There is historical precedent that optically dense natural hazes may exist in this region, as described in the observations reported by the early Spanish explorers and later settlers.

From the prevailing winds, it is expected that air entering the coastal areas of Southern California is "marine" in origin, in the sense that sea salt should make up a significant part of the background aerosol. There are few observations of the properties of aerosols in offshore air. One study by Holzworth (1959) dis-

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cussed results of aerosol sampling in remote sites of coastal California, including two island stations. These data showed anomalously high values of total mass loadings of aerosols, compared with presently available information from other sources. Holzworth's investigation also suggested that the chemical composition of the aerosol sampled was enriched in sulfate and nitrate far beyond that expected from sea salt.

Recently, Blifford (1970) and Gillette and Blifford (1971) have reported a few measurements of aerosols 250 km offshore from Santa Barbara. Their filter samples taken in 1967 near the ocean's surface have shown low sodium and chlorine content but high sulfur and calcium content. Further, they found significant traces of silicon in these samples, indicating contributions from continental air masses.

To supplement previous observations of aerosol properties in the California coastal atmosphere, we undertook during 1970 a new study of San Nicolas island (SNI) located ~130 km west-southwest of Los Angeles. The objectives of this study were to (i) characterize the offshore background aerosol in terms of physical and chemical properties under specified meteorological conditions, and (ii) relate the properties of the offshore component to the properties of the Los Angeles aerosol.

The results of the 1970 expedition to San Nicolas Island are described here. They are interpreted in terms of previous results, current knowledge of major sources, and atmospheric processes contributing to the evolution of airborne particles.

## 2. Experimental

San Nicolas Island was chosen as the sampling site because it is the remotest of the Channel Island group west of Southern California. It is located in a zone where the prevaliing winds are from the northwest. Assuming that the aerosol in the marine layer below the inversion base is dominated by local sources, it was expected that the airborne particles on the island would be mainly sea salt with traces of soil dust and organics from the island vegetation and from the sea surface. Past work has indicated that islands are less than ideal sites for characterizing aerosols over the sea. With this reservation the observations are presented in subsequent sections.

San Nicolas Island is a barren, rocky hillock rising 275 m maximum out of the sea. Its climate is arid except during the winter when it normally experiences traces of precipitation. Because this island has borne the brunt of persistent offshore storms for centuries, it is largely swept clean of loose finely divided soil and now has a surface mainly of decomposing sandstone. There is only sparse vegetation as a variety of weeds including buckthorn grass, iceplant, and a few species of cactus. The island is populated with about 100 people, representing part of the U. S. Navy's operational arm of the Pacific Missile Range. The anthropogenic activity is concentrated on the southeast part of the island.

TABLE 1. Instrumentation and meteorological support for the experiment.

| Aerosol instrumentation | Sampling mode |
|---|---|
| General Electric Continuous Aitken Nucleus Counter | Continuous |
| Royco 225 Optical Counter | Continuous |
| Meteorology Research Inc. Model 1550 Integrating Nephelometer | Continuous (summer only) |
| High-volume filter sampler (National Air Surveillance Network design) | Intermittent, 24-hr samples |
| AIHL 2-stage low-volume filter | Intermittent, 24-hr samples |
| **Meteorological support*** | **Sampling mode** |
| Surface wind (magnitude and direction) temperature, relative humidity | Three sites on island, continuous |
| Rawinsondes [winds (magnitude and direction), temperature, dew-point to upper troposphere] | Twice a day from SNI and Pt. Mugu |
| Visibility | Hourly, visual and transmissometer |
| Oxidant (electrochemical-NOAA ozonesonde) | Intermittent at SNI |

* Supplied by Pacific Missile Range (PMR) weather unit.

### *a. Sampling and instrumentation*

The main sampling location chosen was on the remote northwest side of the island at ~200 m altitude. The site chosen was a shed located about 20 m to the windward side of a gravel access road. This portion of SNI is restricted and is not often frequented by the island personnel, except for testing operations. A meteorological tower is located about 30 m northwest of the balloon shed. Here wind data were obtained. The area below and to the windward of the site is primarily eroded and partially decomposed sandstone formations followed at a distance by sand dunes.

To check the representativeness of the samples at the balloon shed, a few observations were made 1 km south of the base complex near the island power plant. Limited observations were also taken about 3 m above the sea in the spray zone along the northwest shore.

Listed in Table 1 are the various instruments used in the study with their sampling schedule. Sampling was conducted during two periods, the first from 28 July to 13 August, 1970, and the second from 6–22 October 1970. Observations of physical properties were made both on a continuous and an intermittent basis, while the samples for chemical analysis were collected intermittently for 24-hr periods using filters with approximately 99% collection efficiency for particles reaching the filter surface.

Except for the filter samples, all of the instrumentation was located most of the time in the balloon shed. For the Aitken nucleui counter and the Royco optical counter, the sampling was conducted through a 5-cm diameter plastic (PVC) pipe extending 7 m above the ground and 2 m above the roof of the shed. The nephelometer sampling was made through a 3-cm diameter vacuum cleaner hose with inlet located 3 m above the ground. There was no humidity control on the inlets of the Aitken nuclei counter or the Royco 225 counter. However, the nephelometer inlet was equipped with an air heater to reduce the relative humidity of the sampled air below 70%.

The two filter samplers were located on a concrete pad at the base of the meteorological tower 30 m NW of the balloon shed. The high-volume filter sampler was placed in a standard National Air Surveillance Network housing, standing ~1 m off the ground. The AIHL two-stage sampler (Mueller and Imada, 1969) was oriented such that the filters were facing directly away from the prevailing wind.

TABLE 2. Summary of chemical analyses undertaken on filter collected samples.

| Method | Reference |
|---|---|
| Colorimetry | |
| $NH_4^+$ | Extraction procedure: USPHS (1965) |
| $NO_3^-$ | Analytical procedure: Snell and Snell (1936) |
| Flame photometry | |
| Na | APHA (1971) |
| Gas chromatography | |
| non $CO_3^=$ carbon | Air & Industrial Hygiene Laboratory (1971) |
| Gravimetry | |
| Total ash at 450C; weigh residue | |
| Solvent extraction | |
| Organics (cyclohexane soluble) | DuBois *et al.* (1970) |
| Turbidimetry | |
| $Cl^-$ (water soluble) | USPHS (1958) |
| $SO_4^=$ (water soluble) | USPHS (1965) |
| Alpha excited x-ray emission | |
| Ca | Flocchini *et al.* (1972) |
| Cu | |
| Fe | |
| K | |
| Pb | |
| Si | |
| Zn | |
| X-ray fluorescence | |
| Al | Preliminary result by x-ray excited fluorescence system similar to apparatus described by Jaklevic and Goulding (1971). |
| Br | |
| Cr | |
| Mn | |
| Ti | |

*b. Filter sampling and chemical analysis*

The total mass concentration of aerosol samples was obtained from weights on 2.5-cm diameter glass fiber filters (Gelman Type A). Prior to use, these filters were washed in 8 molar $HNO_3$ and were rinsed in de-ionized water. The 2.5-cm filters were mounted in the AIHL two-stage sampler which classifies the aerosol into total mass concentration and a refined fraction consisting of particles $<3.5$ μm diameter.[6]

The carbon content of the sampled aerosol was determined from the total mass on the glass fiber filters.

For the remaining chemical analysis, high-volume filter samples were taken using the hi-vol sampler with 27.9 cm×21.5 cm TFA-810 cellulose filter paper. The series of analyses carried out on the filters are listed in Table 2. References are given for the analytical procedures used.

The cellulose filter sheets to be analyzed were cut in half. One-half sheet of the cellulose filter mat was first extracted for 6 hr with cyclohexane, and the organics were determined by weight after evaporation of the solvent under nitrogen. The half-sheet was then extracted with water. Aliquots of the water extract were then analyzed for chloride turbidmetrically using barium chloride; nitrates and ammonium were analyzed colorimetrically. Another aliquot of the water extract was taken to determine sodium by flame photometry.

The remaining half-sheet was retained for other analyses including elemental analysis by alpha-excited x-ray emission spectroscopy at University of California, Davis, and x-ray fluorescence analysis at Lawrence Berkeley Laboratory. A 2-cm disc was cut from the remainder of the second half-sheet and was ashed by heating for 4 hr at 450C. The remainder after ashing was considered to be the non-volatile part of the aerosol; the volatiles must have included carbonaceous material and water. Probably other compounds are volatilized, such as ammonium salts, and some of the non-volatiles may be oxidized to higher valence states. However, to the authors' knowledge, no detailed studies have been conducted on this question.

Classification of the cyclohexane soluble materials was attempted into paraffinic and oxygenated components. However, the amount of solvent soluble matter extracted was too small for a satisfactory fractionation by the methods employed.

## 3. Experimental results

The observations of temperature, relative humidity, wind speed and direction, and visibility taken during the experiment are summarized in Tables 3 and 4. The data in Table 3 represent the overall average conditions for the summer and fall periods. In Table 4, average conditions during both periods are shown for

[6] The cyclone classifier removed particles of 3.5-μm diameter with a 50% efficiency. Larger particles were removed at correspondingly greater efficiencies.

TABLE 3. Summary average meteorological observations on San Nicolas Island.

| | July–August | October |
|---|---|---|
| Temperature (°C) | 17.3 | 14.2 |
| Relative humidity (%) | 86 | 99 |
| Wind direction (deg) | 270–330 | 290–340 |
| Wind speed (km $hr^{-1}$) | 9.3 | 8.8 |
| Visibility (km) | 14 | 19 |
| Inversion base (m) | 440 | 960 |
| Oxidant (pphm)* | 5 | 8 |

* Oxidant detected by the ozonesonde measures primarily ozone but is subject to large interference by $NO_2$.

three classes of wind vectors as measured on the island. The classes were identified as marine enriched, restricted by winds from directions 180° to 300°; coastal-marine, with wind directions 300°–360°; and continental enriched, with wind directions 0° or 180°. Little difference in averaged meteorological properties was detected except that the visibility in air from the western zone may have been slightly better in October than air coming into the island from onshore directions. The data taken indicated that the summer sampling period was characteristic of offshore climatological conditions, with light winds and diurnal changes characterized by 1) stratus clouds at night and morning, often dispersing by mid-day, and 2) a temperature-humidity cycle such that relative humidities increased in the evening, remaining at 100% through the night to mid-morning. The conditions were very stable and the same throughout this period, with one day of particular interest on 30 July 1970 where the inversion base dropped to just below the altitude of the higher portions of the island.

The sampling conditions during October were more interesting meteorologically. In this case, the period of transitional offshore flow between summer and winter was marked by a well-documented case of penetration of air over SNI from continental sources in Southern California as a result of a light easterly drift of air over 7–9 October. This condition was marked by a significant decrease in humidity on the island, accompanied by an increase in oxidant level. Later, on 20 October, a weak storm front moved southward over the island yielding light rain (<1 mm) during its passage. During the period between 9 and 18 October, a heavy haze persisted over the coastal waters, well beyond the Channel Islands.

### *a. Aerosol measurements*

The averaged aerosol properties measured over the two periods of observation are shown in Table 5. The averages for the three air mass classifications are listed in Table 6. There is little difference in the observations over the period studied except in the large particle fraction. The Aitken nuclei concentrations would suggest that the aerosol sampled was not pure marine air, on the average, because the counts were at as much as a factor of 5 too high compared with observations of 200–600 $cm^{-3}$ reported over the mid-ocean. Instead, the samples evidently represented a mixture of aged material from both marine and continental sources.

The nephelometer observations indicated that the particle concentration in the light-scattering range (diameters approximately 0.1–1.0 $\mu$m) were low, with average light scattering approaching the noise level of the instrument. Since the air entering the nephelometer was pre-heated to reduce the air humidity below 70%, the nephelometer should show little correspondence with visibility measurements when humidity is a significant factor. This was found to be true for the July period where the linear correlation between the two observations was found to be insignificant.

The measurements of particles larger than ~0.5 $\mu$m diameter using the Royco optical counter displayed a wider range of variability than the nephelometer. The concentrations of larger particles generally were similar to other observations of aerosols at remote sites. Evaluation of the data for larger particles indicated that the number distribution of particles measured on the island qualitatively was consistent with those observed over the Atlantic Ocean by Junge and Jaenicke (1971), and with Blifford's observations over the eastern Pacific Ocean only for particles of diameters >2 $\mu$m. Below this diameter, the optical counter qualitatively detected significantly more particles than expected from Blifford's impactor data, taken 0.015 km above the ocean in an aircraft. It should be borne in mind, however, that the Royco instrument used in this study provided only semi-quantiatative data for the

TABLE 4. Classification of SNI meteorological observations by wind direction.

| | July–August | | | October | | |
|---|---|---|---|---|---|---|
| | Continental enriched | Marine enriched | Coastal marine | Continental enriched | Marine enriched | Coastal marine |
| Wind direction (deg) | 0–180 | 180–300 | 300–360 | 0–180 | 180–300 | 300–360 |
| Temperature (°C) | 17.4 | 17.2 | 17.5 | 13.7 | 14.7 | 14.1 |
| Relative humidity (%) | 82 | 88.3 | 89.3 | 93.6 | 86.1 | 99 |
| Wind speed (km $hr^{-1}$) | 9.8 | 7.9 | 6.8 | 10.1 | 7.0 | 9.3 |
| Visibility (km)* | 15 | 13 | 14 | 16 | 29 | 17 |

* Visual observation from PMR weather station at south end of Island. Ranging beyond ~5–10 km is qualitative because of insufficient targets; beyond ~30 km the nearest inshore island is visible.

TABLE 5. Overall averaged properties of aerosols measured on San Nicolas Island.

| | July–August | October |
|---|---|---|
| Aitken nuclei concentration (number $cm^{-3}$) | 2400 | 2600 |
| Particles $>0.5\ \mu m$ diameter (number $cm^{-3}$) | 30 | 93 |
| $b_{scat} \times (10^4\ m^{-1})$ [c] | 0.5 | – |
| Total mass concentration ($\mu g\ m^{-3}$) [a] | 29.8 | |
| Refined mass concentration ($\mu g\ m^{-3}$) [b] | 12.1 | |

[a] Average of 22 glass fiber filter samples excluding one taken at the spray zone, which was 79.8 $\mu g\ m^{-3}$.
[b] Average of 22 glass fiber filter samples, excluding one taken at the spray zone, which was 16.6 $\mu g\ m^{-3}$. Refined mass covers particles $\lesssim 3.5\ \mu m$ diameter at 50% removal efficiency.
[c] Inlet air at $\lesssim 70\%$ relative humidity.

aerosol size distribution for particles $>0.5\ \mu m$. This instrument, through its optical design, is insensitive to resolving number concentration over the particle diameter range between 0.6 and 1 $\mu m$.

Calculating the average diurnal variation of the particle counters suggested no systematic changes in the Aitken nuclei population or the total light scattering. However, the Royco counter displayed a diurnal pattern with maxima at night and minima at mid-day. This followed qualitatively the relative humidity variation, but showed an insignificant linear correlation between the two variables.

### b. *Total mass concentration*

The determinations of mass concentration from the high-volume sampler results were systematically higher than the low-volume sampler data. However, the cellulose filters are known to be exceedingly susceptible to weight change with changes in humidity, while the glass fiber substrate suffers considerably less from this potential error. Since the procedures for the cellulose filters were not well controlled at the time of weighing, the low-vol data using the glass fiber filters are believed to be superior to the cellulose medium used in the hi-vol sampler. Therefore, the mass concentration derived from the glass fiber substrate has been adopted to reflect the most accurate mass concentrations. This choice is made with reservation, however, because of the orientation of the low-vol units away from the wind. Such an orientation may have led to an anomalously low sampling efficiency of large particles compared with the hi-vol device. Yet, this is unlikely to be a major error since comparison between the total mass collected by the low-vol sampler and the refined fraction gives a ratio between the two which is reasonable with respect to subsequent experiments.

The levels of mass concentration as determined from the glass fiber filter weights were found to be at levels characteristic of remote sites (see, for example, Spirtas and Levin, 1970). The observations were about one-third or less of the annual averaged mass concentrations in Los Angeles. The total mass and refined mass derived from the AIHL two-stage filter sampler showed the mass concentration of smaller particles was only about 40% of the total mass concentration of particles. This is in contrast to data taken under conditions of moderate-to-heavy smog in Pasadena in 1969 that indicated the refined fraction was larger than half of the total. The lowest mass concentrations were observed after passage of the weak storm front in October, whereas the highest values were associated with the east wind conditions.

The total mass concentrations were significantly lower than those reported by Holzworth (1959), who measured averages of 90 $\mu g\ m^{-3}$ on San Nicolas Island. It is not clear why this discrepancy exists. It may be related to (i) the sampling location of the earlier study, which was located downwind of the residential complex and near the airfield, (ii) differences in wind speed conditions during the observations, or (iii) differences in sampling efficiency of the two-stage sampler and the high-volume sampler.

### c. *Chemical properties*

The averaged results of the chemical analysis of the samples taken on San Nicolas Island are summarized in Table 7. The percentages shown have been calculated on the basis of the mass concentration estimated from the glass fiber filters despite the fact that most of the analysis was derived from the cellulose substrate. This choice has been made on the basis of the conclusions summarized above in regard to the total mass concentrations. The overall average concentration of selected

TABLE 6. Classification of aerosol measurement by wind direction.

| | July–August | | | October | | |
|---|---|---|---|---|---|---|
| | Continental enriched | Marine enriched | Coastal marine | Continental enriched | Marine enriched | Coastal marine |
| Wind direction (deg) | 0–180 | 180–300 | 300–360 | 0–180 | 180–300 | 300–360 |
| Aitken nuclei concentration (number $cm^{-3}$) | 2800 | 2500 | 2400 | 2600 | 2800 | 2500 |
| Particles $\gtrsim 0.5\mu m$ diameter (number $cm^{-3}$) | 20 | 30 | 20 | 50 | 70 | 110 |
| $b_{scat} \times (10^4 m^{-1})$ | 0.6 | 0.5 | 0.4 | — | — | — |

elements and constituents suggests that sea salt is a relatively minor constituent of the sampled aerosol. Silicon, presumably in the form of sand and soil dust, was found at approximately equal concentrations with chloride. There were significant amounts of sulfate and nitrate in the sampled aerosol, but the organic fraction, as cyclohexane extractables, is small in comparison with the benzene-soluble fraction often observed on land. The organic fraction as determined by cyclohexane solubles was substantiated by the total carbon analysis, which generally agreed qualitatively with the solvent-extractable fraction. However, the total carbon recovered was somewhat larger, on the average, than the solvent-extracted material. The difference is associated with cyclohexane-insoluble material, and the difference in number of samples used in averaging (see Table 8). No detectable trace of carbonate carbon was found in the samples by the gas chromatographic analysis. The elements heavier than chlorine, as detected, were found to represent under 5% of the total sample.

The total amount of material specifically accounted for in the analysis averages 56.1%, including carbon. On the other hand, the average total ash content was found to be 74.6%. Noting that the material accounted for, exclusive of carbon, was 53.1%, this non-volatile fraction represented 71% of the total ash, on the average. The remainder not accounted for is believed to be partly oxygen. The direct comparison between the ash content and an analysis of (assumed) non-volatile constituents has not been established, as yet. However, it is likely to be somewhat uncertain because of the potential for loss on ignition of some materials like ammonium salts, but gain in weight may take place by oxidation.

The chemical analysis of several individual samples is shown in Table 8. In the case of sample SN-11 where the AIHL (wet chemical) chlorine determination was missing, the level was estimated from x-ray fluorescence and alpha-excited x-ray emission (XFRA) determinations. For all the samples, the x-ray fluorescence method yielded values somewhat lower than those obtained by the AIHL techniques for Cl, and the alpha-excited method ran higher. Therefore, in the case of this one missing datum, the composite is considered to be a reasonable estimate of what would have been the AIHL determination.

To test the representativeness of analysis on parts of the hi-vol filter, sections were cut from the center (A) and outer edges of a half-filter. Differences between the two x-ray methods were compared on piece (A). The two methods yielded comparable results, except for Si, Cu and Pb when the alpha-excited determinations were significantly higher than the x-ray fluorescence data.

To avoid non-uniformity of deposit, the average of A and B sections was used preferentially as in the case of Br. For Al, Ti, Cr and Mn, only the x-ray fluorescence method is available, based on (A).

TABLE 7. Overall averaged analysis for chemical constituents of SNI aerosol.

| Constituent | Percent by weight[a] | |
|---|---|---|
| Al | 2.8 (±50%) | |
| Si | 5.0 (±50%) | |
| Na | 3.6 (±5%) | |
| P | N.D.[b] | |
| Cl | 9.9 (±10%) | |
| K | 1.3 (±25%) | |
| Ca | 1.9 (±25%) | |
| Ti | 0.15 (±20%) | |
| V | N.D. | |
| Cr | 0.02 (±20%) | |
| Mn | .04 (±20%) | |
| Fe | 1.6 (±20%) | |
| Cu | 0.6 (±20%) | |
| Zn | 0.2 (±20%) | |
| Br | 0.2 (±20%) | |
| Pb | 0.4 (±20%) | |
| I | N.D. | |
| $SO_4^=$ | 17.5 (±10%) | |
| $NO_3^-$ | 5.7 (±10%) | |
| $NH_4^+$ | 2.2 (±10%) | |
| Total inorganics accounted for | 53.1 | |
| Cyclohexane soluble (organics) | | 2.0 (±10%) |
| Non-carbonate carbon | 3.0 | |
| Sum of constituents | 56.1 | |
| Total ash content (TAC) | 74.6 | |
| Loss on ignition (100—TAC) | 25.4 | |

[a] Percentage in parentheses is error estimated by analyst; x-ray fluorescence for $\alpha$-particle excitation only.
[b] N.D. is less than minimum detectable concentration.

The error limits shown in Table 7 are based on Cahill's estimate obtained with the alpha-excited x-ray emission. For the x-ray fluorescence method, no information was available. It is assumed that the error range is similar to that obtained by the alpha-excited method.

Note that the chlorine is determined as water-soluble chlorides. Chlorine occurring in other forms would not have been measured.

The sulfur was determined to the extent that it represented the water-soluble sulfates. The sulfate content made up the major constituent of the samples. The sulfur analyzed may also include sulfites, which are oxidized to sulfate inadvertently during the analytical processing. But there are also Ca and Pb sulfates which are not very soluble in water, nor are some minerals containing S. Thus, the degree to which the soluble $SO_4^=$ represents total S content remains unknown.

The data indicated that the chloride-to-sodium ratio was generally larger than that expected for sea salt. The highest ratios were detected for the period when the inversion base was at the level of the island or below and just after the passage of the storm front. The lowest values were found during the period when considerable

TABLE 8. Tabulation of chemical analysis for individual SNI aerosol samples (weight percent normalized to glass fiber filter mass concentration)[a]

| Sampling no. | Date | Mass concentration[b] ($\mu g\ m^{-3}$) Total | 3.5 $\mu m$ diameter | Percent of total mass Al | Si | Na | Cl | K | Ca | Ti | Cr | Mn | Fe | Cu | Zn | Br |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SN-1 | 7/28–29 | 17.1 | 6.0 | 3.9 | 6.7 | 2.0 | 3.3 | 0.35 | 3.5 | 0.10 | <0.02 | 0.02 | 1.8 | 0.4 | 0.3 | 0.2 |
| SN-2 | 7/29–30 | 17.4 | 3.9 | 4.6 | 4.7 | 3.7 | 10.3 | 2.6 | 1.8 | 0.15 | <0.02 | <0.02 | 0.58 | 0.29 | <0.10 | 0.17 |
| SN-3 | 7/30–31 | 28.8 | 9.0 | 2.8 | 3.3 | 5.9 | 25.3 | 0.5 | 2.7 | 0.03 | <0.01 | <0.01 | 0.36 | <0.06 | <0.06 | 0.23 |
| SN-4 | 7/31–8/1 | 21.7 | 8.6 | 6.9 | 9.7 | 6.4 | 23.8 | 2.5 | 3.5 | 0.09 | <0.06 | <0.06 | 3.32 | <0.10 | <0.10 | 0.37 |
| SN-8 | 8/4–6 | 27.8 | 10.9 | 1.4 | 5.5 | 3.1 | 2.6 | 1.3 | 1.1 | 0.11 | 0.02 | 0.06 | 1.7 | 0.66 | 0.63 | 0.24 |
| SN-11 | 8/12–13 | 26.8 | 15.5 | 3.8 | 2.1 | 0.41 | 0.78 | 0.74 | 0.52 | 0.18 | <0.02 | 0.03 | 1.9 | 1.5 | 0.11 | 0.22 |
| SN-12[c] | 9/16–18 | (47.4)[c] | — | 1.6 | 2.0 | 2.2 | 1.7 | 0.57 | 0.21 | 0.15 | 0.021 | 0.063 | 1.82 | 0.25 | 0.72 | 0.15 |
| SN-13 | 10/6–7 | 24.9 | 13.1 | 5.0 | 0.49 | 8.2 | 21.0 | 0.72 | 1.2 | 0.07 | 0.03 | <0.03 | 0.65 | 0.22 | 0.22 | 0.26 |
| SN-14 | 10/7–8 | 64.4 | 18.3 | 2.0 | 3.3 | 2.1 | 2.3 | 0.45 | 1.1 | 0.26 | <0.02 | 0.09 | 3.6 | 0.06 | 0.38 | 0.16 |
| SN-19[c] | 10/14–15 | (36.6)[c] | 16.6 | 0.23 | 7.1 | 1.8 | 1.0 | 2.1 | 2.2 | 0.11 | 0.028 | 0.057 | 1.1 | 0.28 | 0.11 | 0.20 |
| SN-20 | 10/15–19 | 41.8 | 23.8 | 1.03 | 6.8 | 1.2 | 0.30 | 0.76 | 1.2 | 0.09 | 0.02 | 0.05 | 1.0 | 0.20 | 0.10 | 0.18 |
| SN-21 | 10/19–20 | 18.6 | 9.7 | 3.2 | 9.2 | 4.0 | 8.4 | 3.0 | 3.1 | 0.13 | 0.04 | 0.09 | 1.86 | 1.46 | <.017 | 0.31 |
| SN-22 | 10/20–22 | 12.1 | 2.6 | <1.5 | 3.7 | 5.0 | 27.4 | 0.8 | 2.7 | 0.08 | 0.03 | <0.010 | 1.29 | 2.5 | 0.16 | 0.24 |

[a] Percentages preceded by > signify values not detectable by XRFA at level shown.
[b] Glass fiber filter.
[c] Weight fractions based on cellulose filter weight difference; numbers in parentheses are mass concentration based on hi-vol sample.

amounts of continental air passed into offshore waters with the easterly wind drift.

The sulfate and ammonia concentrations varied in an uncorrelated way with air masses, but high Mn, Si, Pb, Ca, Fe, Zn and $NO_3^-$ concentrations were detected with the air in the eastward moving air mass on 7–9 October 1970. It is interesting to note that the Cl/Na ratios $<1.8$ (sea salt) are all associated with the highest lead concentrations. Atmospheric lead, of course, is believed to be identified mainly with auto exhaust.

## 4. Discussion

The evidence from air sampling on San Nicolas Island points to the conclusion that the air traveling inland over coastal waters of the eastern Pacific near Southern California contains a complex mixture of aged aerosols from marine and continental sources, including those of anthropogenic origins. Thus, the aerosol observed at this remote site contains only a small fraction of sea salt, under light wind conditions, based on sodium chloride, with significant traces of silicates, possibly from wind-blown dust from the Island's surface. Major constituents of the aerosols are the materials $SO_4^=$, $NH_4^+$ and $NO_3^-$ that are identified with production of aerosols from gases in the atmosphere.

The complex nature and small fraction of sea salt observed in 1970 support Holzworth's (1959) earlier results, as shown for comparison in Table 9, and in recent data of Gillette and Blifford (1971) in Table 10. Our observations of the fractional content of certain chemical species are consistent with Holzworth's earlier data, and with the later measurements taken over the ocean by aircraft, except for silicon and sulfur. Gillette and Blifford's results for these elements show significantly lower concentrations than our observations, but both elements fall within the range of variations in constituents for our data. Our results may be high in silicon as a result of dust blowing from the island surface. However, the difference in sulfur content may be associated with differences in sampling procedure, or variations in mixing of polluted air masses offshore of the coast at different times of the year.

### *a. The chloride-to-sodium weight ratio*

Of particular interest in the Gillette and Blifford data is the high Cl/Na ratio of 4.0, 0.015 km above the sea, compared to the value of 1.8 for sea water. Our experiments showed a wide range of Cl/Na ratios, with a value of 2.4 based on the ratio of the average concentration ($\mu g\ m^{-3}$) of these constituents. Again this is significantly larger than sea water though not as large as the Gillette and Blifford result. These investigators attributed their anomalously high ratio to anthropogenic sources of Cl. Our data indicate no local sources for enrichment of Cl; in fact, the air masses with relatively high pollution, as identified with lead, show low Cl/Na ratios. It is important to note, however, that Junge (1963) reported a Cl/Na$<1.8$ for continental aerosols even in coastal areas where both urban and non-urban conditions are prevalent. These data were derived from rainwater chemistry, as well as direct analysis of filtered aerosols. Later data of the National Precipitation Sampling Network (Lodge *et al.*, 1968) showed similar results; a notable exception was an average value of 2.1 from rainwater on Catalina Island off the Pacific coast at Los Angeles.

Recent data of Mueller *et al.* (see Miller *et al.*, 1972) and a review of earlier results (Hidy and Friedlander,

TABLE 8 (*continued*).

| Percent of total mass | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Pb | $NO_3^-$ | $NH_4^+$ | $SO_4^=$ | Organics | C[b] | Total (%) Ash Content | Oxidant (pphm) | Sum of constituents excluding carbon | Remarks |
| <0.5 | 6.9 | 5.8 | 18.1 | 4.2 | 3.7 | — | | 53.5 | |
| <0.4 | 6.3 | 0.9 | 15.7 | 2.3 | — | 74.4 | | 52.4 | Light winds, scattered stratus |
| <0.36 | 2.3 | 0.34 | 11.4 | 1.9 | 1.9 | 82.2 | | 53.9 | Inversion below island top on 7/30. |
| <0.9 | 5.7 | 0.27 | 15.8 | 1.7 | 0.7 | 98.8 | | 74.6 | |
| 0.96 | 5.9 | 2.6 | 21.2 | 1.3 | — | 59.0 | 7.4(8/5), 3.1(8/6) | 48.0 | Low scattered stratus, haze |
| 0.63 | 5.8 | 6.9 | 49.4 | 4.5 | 4.5 | — | 6.1 | 74.8 | Fog over NW and of SNI (low NaCl) |
| 1.6 | 5.3 | 1.6 | 10.9 | 1.7 | — | — | | 30.9 | Only hi-vol filter sample taken |
| 0.26 | 7.6 | 0.39 | 11.5 | 0.8 | 3.9 | 84.0 | | 56.4 | Overcast, cloud base ~600 m |
| 0.44 | 8.0 | 1.6 | 9.1 | 1.9 | — | — | | 34.6 | East wind conditions, scattered stratocumulus base ~300m. |
| 0.63 | 6.8 | 0.92 | 19.2 | 2.8 | 2.8[x] | — | 4.4(10/13) | 46.8 | Very clear (30 mi visibility) high cirrus |
| 0.55 | 2.9 | 2.9 | 14.3 | 2.5 | 4.3 | 43.9 | | 33.7 | Overcast, very light winds |
| 0.22 | 9.6 | 1.9 | 21.1 | 0.0 | — | — | | 65.5 | Overcast, calm, fog over sea |
| <0.16 | 0.40 | 0.24 | 10.2 | 1.2 | — | 79.6 | | 54.1 | Passage of a weak storm front (8/20–8/22) very clear, >30 mi visibility, streaks of cirrus |

1971) of aerosols sampled in Pasadena indicate a Cl/Na ratio $<1$ in polluted air along the southern California coast. In Los Angeles it has been found to be as low as 0.07. In the San Francisco Bay area, a range has been observed depending on conditions of pollution and distance from the ocean. For example, one day's observations in San Francisco gave a Cl/Na ratio of 1.2 (John *et al.*, 1972). In Livermore, values ranging from 0.8 to 1.6 were found (Rahn *et al.*, 1971). Yet in Benicia, Calif., near a refinery and metal smelting complex, Cl/Na ratios as high as 5 were observed by John *et al.*

An anomalously high Cl/Na ratio of 3.5 for aerosols in marine air was found during 30-kt westerly winds in winter 1971 at the Pt. Reyes Lighthouse northwest of San Francisco. This result further suggests that high Cl/Na ratios are not uncommon in unpolluted, marine air along the Pacific coast, north of San Nicolas Island.

Although the SNI data show an average Cl/Na ratio of 2.4, Table 8 shows two cases exceeding 4 (SN-3, SN-22). The meteorological conditions for observing these two cases were special in that neither can be related to penetration of locally polluted air from coastal areas. The first case involved a particularly low inversion base where sampling on the high plateau of the Island was likely to detect a very old or aged aerosol in air subsiding above the marine layer. The second case was associated with an atmospheric disturbance involving the passage of a weak front, creating conditions of light precipitation and relatively deep vertical mixing in the marine layer.

The analytical methods used in this study and potential interferences were evaluated. The known possible interferences in analytical procedure could not account for the Cl/Na results.

Assuming that the methods were correct, the source of the change in Cl/Na ratio along the Pacific coast may involve one or more of several alternatives: 1) fractionation of ions with air-sea boundary processes in forming particles, 2) gain in particulate Cl from continental sources, 3) loss of Na by an unknown chemical reaction of particles, 4) gain in Na from continental sources, 5) gain in Cl by absorption of

TABLE 9. Comparison between SNI data and the result of Holzworth (1959), based on weight percent.

| Constituent | SNI—1970 | SNI—1956–57[b] | S. E. Farallon Island—1956[a,c] |
|---|---|---|---|
| C | 9.9 | 5.5 | 30.3 |
| $SO_4^=$ | 17.5 | 10.7 | 8.9 |
| $NO_3^-$ | 5.7 | 3.6 | 1.3 |
| Organics | 2.0 | 6.1[d] | 3.2[d] |

[a] S. E. Farallon Island is 35 km west of the Golden Gate entrance to San Francisco Bay.
[b] Based on an average of 90 $\mu g\ m^{-3}$.
[c] Based on an average of 142 $\mu g\ m^{-3}$; site at spray zone.
[d] Soluble in $CCl_4$.

TABLE 10. Comparison between SNI data and results of Gillette and Blifford (1971). Data and deviations in $\mu g\ m^{-3}$.

| Element | SNI—1970 | Pacific offshore[a] |
|---|---|---|
| Cl | 2.2 ±3.2 | 1.5 ±0.73 |
| S | 1.7 ±1.7 | 0.24±0.14 |
| K | 0.34± .36 | 0.34±0.10 |
| Na | 0.92±0.94 | 0.38 |
| Si | 1.4 ±1.5 | 0.48±0.39 |
| Ca | 0.50±0.47 | 0.44±0.35 |
| Ti | 0.05±0.06 | 0.06±0.06 |

[a] Sampled by a aircraft 250 km west of Santa Barbara at 0.015 km height above the sea.

gaseous chlorine compounds, or 6) the release of Cl from aerosols to the gas phase by chemical reaction.

The question of Cl and Na fractionation at the sea surface presently is unresolved. Some recent observations suggest that Cl enrichment may take place relative to Na in "true" marine aerosol (Wilkniss and Bressan, 1972). These authors were unable to measure directly the Cl fractionation, but found ambiguities in results from possible volatilization of aerosol during impactor sampling. Tsunogai *et al.* (1972) have reported cases where the Cl/Na ratios from 2–6 were found in aerosols sampled over the North Pacific. Yet shipboard sampling in other regions of the Pacific failed to show such high ratios compared with sea water. It is surprising that such differences in Cl/Na exist in marine aerosols unless the particle formation process depends on surface properties that differ geographically. These observations apparently are not sufficient to determine the extent of Cl and Na fractionation relative to sea water as a result of the aerosolization process.

Analysis of the possible natural or anthropogenic sources that might increase the sodium or chloride concentration in this geographical area (e.g., Miller et *al.*, 1972) suggest that the sea remains the principal source of these elements. Soil will contribute a significant amount of sodium, but the increase in Cl by identifiable anthropogenic activity, such as from lead halides in gasoline, is small.

The Cl/Na ratio could be reduced by the attack on NaCl of $H_2SO_4$ to form $Na_2SO_4$ and HCl or the degradation of NaCl in the presence of $NO_2$ and water (see, for example, Junge, 1963; Miller *et al.*, 1972; Rahn *et al.*, 1971). Aside from the release of HCl from NaCl by such reactions, the few surface measurements available indicate concentrations of gaseous chlorine compounds about equal to that contained in the suspended particles.

A major path for the removal of reactive gases in the atmosphere lies in the absorption of such materials in aerosols and hydrometeors (e.g., Hidy, 1973). The absorption of gaseous chlorine compounds may be the explanation for the high Cl/Na ratios in surface aerosol samples along the West Coast. Both HCl and $Cl_2$ are very soluble in water, so that these compounds could be assimilated rapidly in the presence of cations like $NH_4^+$ by (vapor) diffusion-controlled reaction on particles. Such removal would be in competition with processes like the removal of $SO_2$ by oxidation to sulfate in water associated with fog or aerosols. There is some evidence that the $SO_2$ oxidation in particles is rapid and is diffusion controlled. If so, the removal of $SO_2$ in air near the earth's surface should be dominated by $SO_2$ absorption on aerosols rather than a competitive absorption of HCl or $Cl_2$. This is based on the fact that the concentrations of $SO_2$ are much larger near the ground than the (known) halogen concentrations, and the absorption *rate* essentially will be proportional to the concentration in the gas phase. However, at higher altitude, the $SO_2$ concentration is expected to be more nearly the same as the halogen gases, provided the latter becomes vertically well mixed in time This would allow more halogen absorption into aerosols and condensed water at high altitude than near the ground. On such a basis one would expect an increasing Cl/Na ratio with altitude, as an indicator of "aged" air in the middle and upper troposphere. The Gillette and Blifford (1971) data are important in this respect. Chemical analysis reported by these authors for aerosols sampled in the troposphere for 0–9.1 km show a systematically higher Cl/Na ratio than sea water over the coastal Pacific and the central Pacific over Palymra Island, as well as over a western continental location over Death Valley. A similar pattern was found over Chicago, but their data over the Great Plains are ambiguous, and do not show a strong increase of Cl/Na with height.

The anomalies observed in Cl/Na at San Nicolas Island and at other Pacific coast sites where air masses penetrate from offshore then support the hypothesis that the large-scale subsidence associated with the Pacific high creates a downward migration of aerosols from the middle and high troposphere that are enriched in chloride

The comparison with analysis previously mentioned suggests that the dry aerosol, on the average, may have a higher ratio of Cl/Na than rainwater sampled along the Pacific Coast With the limited data available, this aspect of the problem remains a puzzle, though it may be associated with differences in scavenging or nucleation efficiency for particles of different size and composition It is known, of course, that the nucleation process alone removes a relatively small fraction of the total aerosol population, except for purely marine air.

### *b. Natural sources and the Los Angeles aerosol background*

The observations of San Nicolas Island, as supported by results of previous studies, emphasize the complicated nature of "background" aerosols in air to the westward of southern coastal California. Using chemical evidence, it is possible to classify the San Nicolas Island aerosol by major sources. Based on the results in Table 7, for example, sea salt and soil contribute a significant amount to the aerosols sampled on the Island but cannot account for all of the material. If lead is identified mainly with the automobile, this anthropogenic source is small. These first three are essentially primary in nature, representing emissions directly from surface sources. However, there are also secondary sources of particles involving chemical reactions in the atmosphere. Such secondary processes include the oxidation of sulfur-containing gases to form sulfate, and the oxidation of nitrogen oxides to nitrate. The origins of the volatile material making up most of the SNI particles are uncertain except, of course, for water.

To derive a more quantitative estimate of the primary sources, a calculation for the relative contribu-

tions of sea spray and soil can be made following the procedure described by Miller *et al.* (1972). Their method assumes that the relative source contributions may be calculated by balancing the fraction of a given chemical constituent with the product of source strength and the fraction of the constituent in the source. The composition of sea salt and an average soil dust, taken as soil dust representative of the California area was, reviewed by Miller *et al.* No fractionation of elements during the process of suspension is assumed for purposes of this calculation, even though ion fractionation is known to take place in sea salt aerosol formation and also has been documented for suspended soil particles. Using silicon as an indicator for soil dust, the percentage contribution of this source to the SNI aerosol is estimated. With this number, the contribution of sea salt is calculated assuming that the sodium in the aerosols comes solely from the sea and soil dust. The derived fractional contributions of the two sources are then used as an attempt to account for the remaining important constituents found in the SNI samples.

The calculation based on the procedures of Miller *et al.* (1972) is summarized by scaling the various identifiable primary and secondary sources according to chemical constituents, as indicated in Table 11. Although soil and sea salt are contributors, this tabulation suggests that more than a fourth of the material coming from identifiable sources in the offshore aerosol is secondary in nature. Moreover, over one-fifth of the sample is volatile at 450C, on the average, and is not identifiable with carbon.

The prevailing winds over the Los Angeles area bring air masses inland from offshore much of the year. Thus, the offshore aerosol observed on San Nicolas Island should be chemically consistent with the "background" estimated for Los Angeles urban aerosol. This hypothesis can be checked by comparing the SNI material with the "natural" background of the Pasadena aerosol, as calculated by Miller *et al.* (1972). Taking as a basis that the average offshore background mass concentration is 30 $\mu g\ m^{-3}$ and the average Los Angeles (Pasadena) aerosol is 100 $\mu g\ m^{-3}$, the comparison is shown in Fig. 1. Here the offshore background is indicated as a slashed bar, as compared with an estimated natural background of sea salt and soil dust calculated by Miller *et al.* (1972). The SNI samples can account for the estimated background to a deviation of a factor of 2 or less for some of the elements, including Mn, Cl, Na and Fe. The large difference in Cu between the SNI sample and the estimate is believed to be related to copper particles locally generated from the hi-vol sampler motor.

The offshore aerosol is similar to that calculated for a soil-sea salt dominated material over Los Angeles in some respects. However, the comparison in Fig. 1 suggests differences in the "background", particularly with respect to K, Ca, Cl, $SO_4^=$ and $NO_3^-$. Potassium and chlorine, however, appear to be "borderline" cases where the background anomaly may remain within the uncertainty of the calculation. The latter two are associated, at least in part, with chemical transformations in the atmosphere away from localized sources of pollution.

TABLE 11. Contributions by source to SNI aerosols (weight percent).

| | | |
|---|---|---|
| 1. Primary | Soil (based on 25% Si in soil) | 20.0 |
| | Sea salt (based on 30.6% Na in sea salt) | 11.1 |
| | Automobile lead (based on 40% lead in auto emitted aerosol) | 1.0 |
| | Carbon* | 3 |
| 2. Secondary | Sulfate | 17.5 |
| | Ammonium | 2.2 |
| | Nitrate | 5.7 |
| | | 61 |
| 3. Total volatiles other than carbon: [100−(Total ash-carbon)] | | 22 |
| | Total accounted for | 83 |

* Some of this may be produced in the atmosphere by chemical reaction; however, it is identified with primary origin for this estimate.

The influence of pollution in aerosol over Los Angeles is well illustrated in Fig. 1. There is major enrichment in Mn, Ca, Br, Fe, Pb, $SO_4^=$ and $NO_3^-$ over the offshore component that comes from local anthropogenic sources in the Los Angeles Basin. A striking depletion in $Cl^-$ is shown, suggesting the importance of acid gas attack on NaCl to release HCl into the air as a gas.

## 5. Summary and conclusions

The evidence outlined here shows that the aerosol sampled offshore of the Southern California coast is a complicated mixture of aged material coming from natural and anthropogenic sources. These mixtures are expected to be highly variable depending on the large-scale air flow and its perturbations experienced on a mesoscale, particularly in eddying flow around Pt. Conception, north and west of Los Angeles. The heavy hazes often observed over the eastern Pacific within 100 km of Southern California coastal areas are undoubtedly linked with variations in the offshore background aerosol, but they cannot be attributed alone to the exchange of material between the sea and atmosphere. The explanation for the nature of Southern California hazes remains uncertain, but it is clear that a significant contributor to this phenomenon is material coming from transformation of reactive gases to aerosols in the atmosphere.

The essential conclusions of the study are:

1) The average aerosol concentration measured on San Nicolas Island was in the range of 2000 $cm^{-3}$, based on the Aitken nuclei population.

2) The average concentration of particles $>0.5\ \mu m$ diameter was 20–100 $cm^{-3}$.

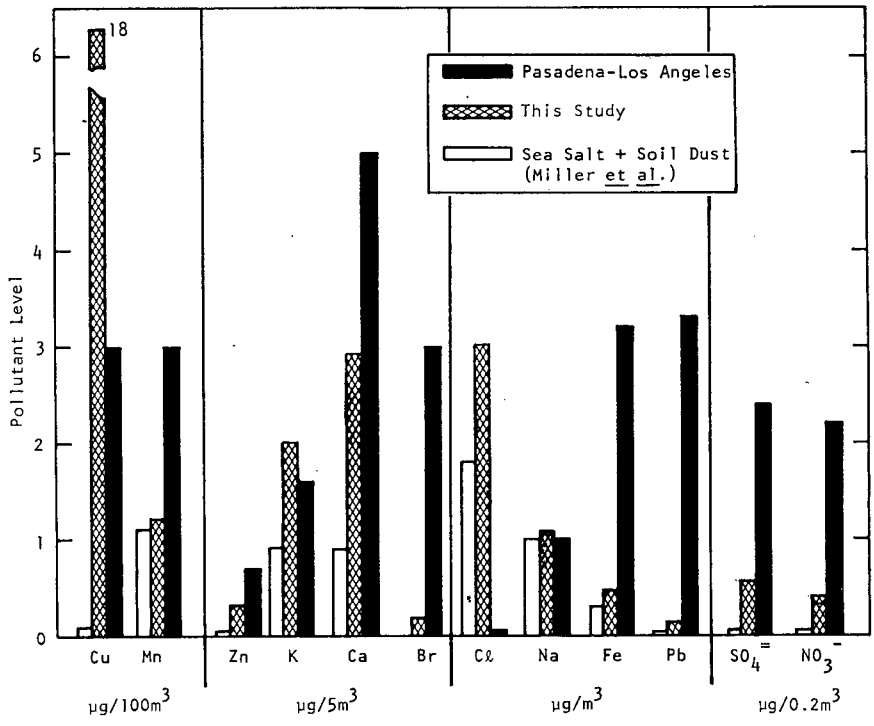


FIG. 1. Comparison between trace material concentration in the Los Angeles atmosphere and the offshore background on San Nicolas Island. Data for average concentrations in Pasadena were based on results in 1969 reported by Miller *et al.* (1972), except for $SO_4^=$ and $NO_3^-$ which are average values from the National Air Surveillance Network.

3) The average mass concentration of aerosols for 22 samples taken in late summer and early fall 1970 was 29.8 $\mu g\ m^{-3}$ with 40% of the sampled material being less than 3.5 $\mu m$ diameter.

4) Chemical analysis indicated that 20% of the material was soil dust based on Si concentration, while approximately 11% was sea salt. More than 25% of the particles was sulfate, nitrate and ammonium, which are constituents that are believed to be produced from gases by atmospheric chemical transformations.

5) The chemical analysis accounts for ~56% of the material sampled. This was estimated to be over 80% of the sample, on the average, if the elemental composition is extrapolated to the composition of common materials including soil dust and sea salt.

6) A Cl/Na ratio of 2.4 based on the average concentration of these constituents was found, which is significantly higher than that of sea water. This high ratio is hypothesized to be related to transformations into the condensed phase of gaseous chlorine compounds.

7) The chemical composition of the aerosol sampled on San Nicolas Island is similar to the background aerosol composition estimated as soil dust and sea salt for the Los Angeles area. The main differences lie in the constituents Ca, Br, Pb, $SO_4^=$, $NO_3^-$.

8) The strong influence of localized pollution in Los Angeles air was illustrated by comparing the SNI aerosol with samples taken in Pasadena and Los Angeles. Anthropogenic sources contribute most strongly to the concentrations of Mn, Ca, Br, Fe, Pb, $SO_4^=$, $NO_3^-$, and non-carbonate carbon. Moreover, the importance of Cl release by attack of acid gases on NaCl-polluted atmospheres is noted.

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